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(71) Applicant

Unisearch Limited

(Australia-New South

Wales)

221-227 Anzac Parade

Kensington

New South Wales 2033

Australia

(72) Inventor

Raymond Gary Simons

(74) Agent and/or Address for

Service

Mewburn Ellis and Co

2/3 Curator Street

London EC4A 1BQ

(54) Bipolar membranes with separate anion and cation exchange films

(57) Low electrical resistance bipolar membranes are prepared by joining together separate anion exchange and cation exchange films characterised in that the interface of the two membranes is chemically treated to incorporate chemical substances into the interface of the two ion exchange regions, whereby the electrical resistance of the resultant bipolar membrane is lowered.

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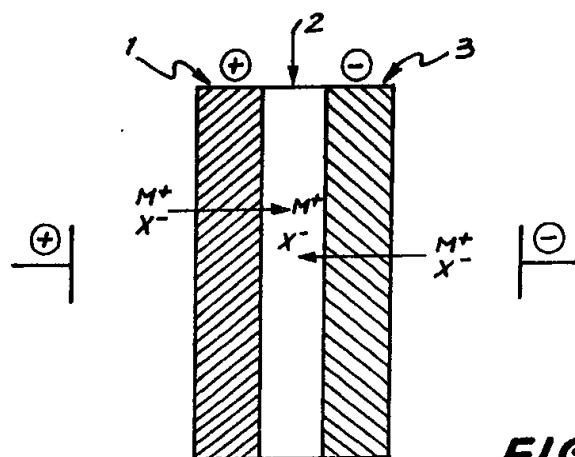


FIG. 1

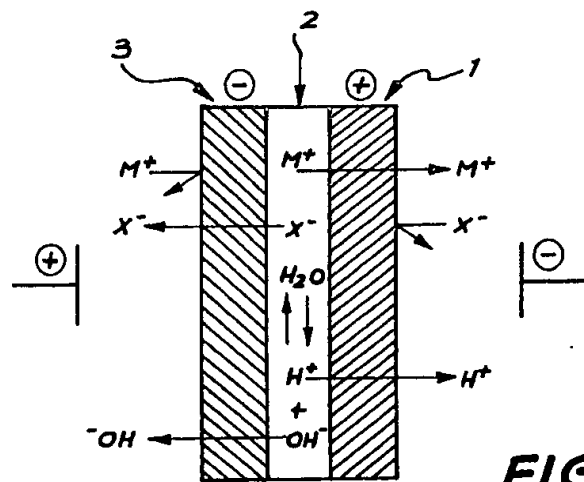
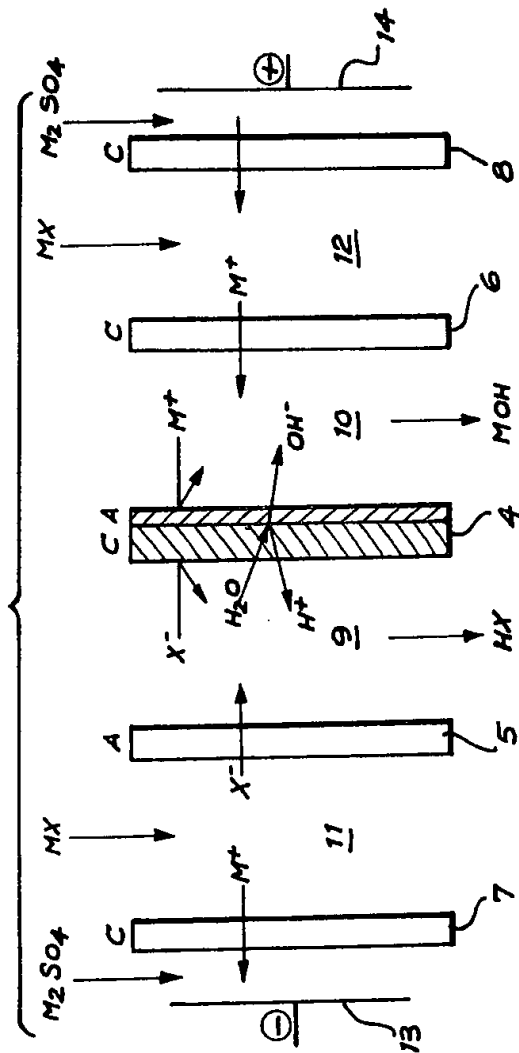


FIG. 2

FIG. 3

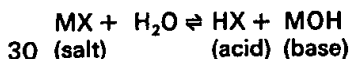


SPECIFICATION

Bipolar membranes with separate anion and cation exchange films

5 The present invention relates to low electrical resistance bipolar membranes comprising separate anion and cation exchange films, to a process of producing same and to the use of such membranes for producing acid and alkali.

10 Acids and bases are important intermediates for a wide variety of products made by the chemical industry. After processing and use these find their way back to nature as salts. A logical route for completing the cycle would be to regenerate the acids and bases directly from these salts. Electrolysis of brine to generate chlorine and caustic soda, in a certain sense, is such a process. Another process is electrodialysis, using bipolar membranes to directly generate acids and bases from their salts. The process is electrically driven and the splitting of the salt to generate the acid and base occurs in an aqueous medium. The process is conceptually a simple one and can be represented by the equation:



To effect and maintain separation of the various species, ion exchange membranes are used. The most crucial of these is the bipolar membrane, so called because it is composed of two distinct parts which are selective to ions of opposite charges. Under the influence of an applied direct current, such a sandwich membrane is capable of forcibly dissociating water to form equivalent amounts of hydrogen and hydroxyl ions. Used in conjunction with other cation- and anion-selective (i.e., monopolar) membranes, the assembly constitutes a potentially economical water splitting apparatus that generates acid and base.

The standard free energy for a process that converts water to one molar hydrogen and hydroxyl ions at 25°C is 19,100 cal/mole. For a reversible process, i.e., a process approaching zero current density, this translates to an energy requirement of 0.022 kWh/mole at 25°C. For production of caustic soda this is equivalent to an energy requirement of 500 kWh/ton. An efficient water splitting system is therefore capable of generating acid and base solutions at a fraction of the costs encountered commercially (2800–3500 kWh/ton).

Bipolar membranes can be prepared by many different methods. In U.S. Patents 4,024,043 and 4,057,481 (both Dege et al) single film bipolar membranes are prepared from pre-swollen films containing a relatively high amount of an insoluble cross-linked aromatic polymer on which highly dissociable

cationic exchange groups are chemically bonded to the aromatic nuclei to a desired depth of the film from one side only; subsequently, highly dissociable anionic exchange groups are chemically bonded to the unreacted aromatic nuclei on the other side of the film.

In Japanese patent publication Nos. 78-158638 and 79-7196 (both Tokuyama Soda Co. Ltd.), bipolar membranes are prepared by partially covering a membrane with a cover film, sulfonating the surface of the membrane not in contact with the cover film to introduce cation exchange groups, exfoliating the cover film, and introducing anion exchange groups on the exfoliated surfaces.

Bipolar membranes have also been prepared by bonding together separate anion and cation exchange films or membranes. The two monopolar membranes of opposite selectivity can be fused together with the application of heat and pressure. See, for example U.S. patent 3,372,101 to Kollsman wherein separate cation and anion membranes are bonded together in a hydraulic press at 150°C at a pressure of 400 lb/sq. inch to form a two ply membrane structure.

However, bipolar membranes formed in this way suffer the disadvantage of high electrical resistance produced by the fusion. Furthermore these membranes are prone to bubble or blister and they are operable for only short time periods at relatively low current densities. These disadvantages make the bipolar membranes formed in this way unattractive for commercial electrodialysis operations.

Thus while the preparation of bipolar membranes from separate anion and cation exchange membranes has been achieved, such bipolar membranes do not display high ion selectivities and yet have low voltage drops at relatively high current densities and electrolyte concentrations.

It is a further object of this invention to provide a method for preparing low resistance bipolar membranes with a high efficiency for water splitting by joining together separate anion and cation exchange membranes.

According to one aspect of the present invention there is provided a process for preparing bipolar membranes comprising joining together separate anion and cation exchange membranes characterised in that the interface of the said membranes is chemically treated to introduce one or more inorganic compounds into the interface of the membranes.

According to another aspect of the present invention there is provided a bipolar membrane comprising separate anion and cation exchange membranes wherein the interface of the two membranes is chemically treated to lower the electrical resistance of the bipolar membrane. More specifically the present invention provides a bipolar membrane comprising an anion exchange region, a cation ex-

change region and an interfacial region containing one or more inorganic compounds and which comprises the surfaces of both said anion and cation exchange regions and the intervening regions therebetween.

5 The bipolar membrane consists of three principle regions:

1. The anion exchange membrane: The prime function of the anion exchange membrane is to pass OH^- ions derived from water splitting at the interface and to exclude cations from the external solution.

10 2. The cation exchange membrane: The prime function of the cation exchange membrane is to pass H^+ ions derived from water splitting at the interface and to exclude anions from the external solution.

15 3. An interfacial section comprising the surface layers of both membranes and the intervening region where they are contiguous: It is in this region that water splitting occurs.

20 The bipolar membranes manufactured in accordance with the teaching of the present invention are characterised in that inorganic compounds are incorporated into the interface of the two ion exchange regions. The inorganic compounds are spread over a surface of one or else both membranes prior to pressing them together. The electrical resistance of the resulting bipolar membrane is usually much smaller than that of a membrane when the interface is untreated. A potential difference across the membrane which is less than 1.1V can be sufficient for a current density of

25 100mA cm^{-2} when it separates 1N KCl solutions. The corresponding voltage for an untreated membrane is likely to exceed 3V. In addition the current efficiency for acid base production of treated membranes is higher than 85%.

30 A wide variety of anion and cation exchange membranes may be used in the invention but preferably the membranes contain sulphonic acid and quaternary ammonium groups.

35 The chemical treatment of the interface between the anion and cation exchange membranes is normally carried out with a substantially aqueous solution of a suitable salt or salts. The solutions not only provide a high degree of bonding and adhesion between the anion and cation exchange membranes but, more importantly, provide a much lower electrical resistance for the resulting bipolar membrane than if the membrane interface was not treated with solution or was bonded simply by the prior art application of heat and pressure.

40 Suitable inorganic compounds or salts for use in the present invention include cations selected from, for example, Group 1a through to Group 4a, inclusive, together with the lanthanides and actinides, in the Periodic Table of Elements, for example Thorium, Zirconium, Iron, Lanthanum, Cobalt, Cadmium, Manganese, Cerium, Molybdenum, Nickel,

Copper, Chromium, Ruthenium, Rhodium, Stannous, Titanium and Indium. Suitable salts for use in the present invention may also include anions such as tetraborate, metaborate, silicate, metasilicate, tungstate, chlorate, phosphate, sulfate, chromate, hydroxyl, carbonate, molybdate, chloroplatinate, chloropalladate, orthovanadate, tellurate and others. It will be appreciated that the above list of suitable anions and cations is not exhaustive. Further, while single salts may be used, mixtures of salts may be used with advantage.

45 Prior to the surface treatment the membranes may be either dry or wet. The surface treatment is accomplished by wetting a surface of one or both membranes with one or more solutions containing selected materials. The anion and cation exchange membranes are then pressed together either at room temperature or else under heat with treated surfaces located at the interface. This heating is carried out at a temperature in the range from ambient up to a temperature just below the onset of deformation or degradation of the anionic or cationic exchange membranes employed.

50 The invention will now be further described in more detail with reference to the drawings in which:-

55 *Figure 1* is a schematic representation of a bipolar membrane according to the present invention;

60 *Figure 2* is a schematic representation of the bipolar membrane of *Fig. 1* with the orientation thereof reversed; and

65 *Figure 3* is a schematic representation of a bipolar membrane for generating an acid and a base from a salt solution.

70 As shown schematically in *Fig. 1*, a bipolar membrane according to the invention consists of three regions, a cation-selective region 1, an anion-selective region 3, and the interface between these two regions 2. These membranes behave anisotropically under the influence of an electric field as is illustrated by the transport processes shown in *Fig. 1*. *Fig. 1* shows that when a direct current is passed across the bipolar membrane with its cation side toward the anode and salt solution on either side, cations and anions are transported to the interface through the permselective membranes, but the passage of ions out of the interface region is limited since they would have to pass through membranes of the wrong selectivity. The salt consequently builds up at the interface and results in a low resistance in this region. When the orientation of the membrane is reversed as shown in *Fig. 2* and a current is passed, salt from the interface is transported to the external solutions leaving only H^+ and OH^- ions from the dissociation of water to carry the current. In this mode the resistance of the interface can become high since water has a low conductivity.

Fig. 2 illustrates the water splitting capacity of the bipolar membrane. If the interface is made very thin, then even though only H^+ and OH^- ions may be present the resistance of the layer can be small and the membrane may be used to generate acid and base.

Literature on the use of bipolar membrane water splitting to generate acid and base dates back at least to the mid-fifties. A general arrangement of the membranes for generating acid and base from salt solution is shown in Fig. 3. It is seen that an arrangement consisting of a cation-selective membrane, a bipolar membrane and an anion-selective membrane serves to keep the acid, base, and salt solutions separated.

As shown in Fig. 3, a bipolar membrane 4 is depicted schematically as a water-splitter in an electrodialysis cell. Acid and base flow through compartments on opposite sides 9 and 10 of the bipolar membrane 4, which are also bounded by anion permeable and cation permeable ion exchange membranes 5 and 6, respectively. Salt solution, MX passes through the adjacent compartments 11 and 12 which are separated from the electrode compartments 13 and 14, containing a salt solution such as M_2SO_4 solution, by additional cation exchange membranes 7 and 8. Under the influence of a direct electric current, anions (X^-) and cations (M^+) within the bipolar membrane migrate out of the membrane toward the anode and cathode, respectively, and in the vicinity of the interface their concentrations rapidly decline. At this point continued passage of the electric current can only occur by the transfer of OH^- and H^+ ions produced by the dissociation of water ("water-splitting") at the interface. Naturally, the membranes must be sufficiently water permeable in order to replace water molecules consumed by the reaction; otherwise the membrane will "burn-out".

The six compartments 9, 10, 11, 12, 13, and 14, separated by five membranes 4, 5, 6, 7 and 8, together constitute a cell unit. A large number of such cell units can be assembled to form an electrodialysis stack. Direct current input to the stack is made via the two electrodes at the ends of the stack.

The invention will now be further described by reference to the Examples.

EXAMPLE 1

Negev Institute anion and cation exchange membranes were dipped into 10% solution of ferric chloride and pressed together at room temperature. The potential difference across the bipolar membrane when it separated 1M KCl solutions at room temperature was 1.7 volts when the current was 100 mA cm^{-2} . The current efficiency for acid base production exceeded 85%. By comparison the voltage across a bipolar membrane formed from the same unipolar membranes, at the same cur-

rent and electrolyte concentration, was 3 volts.

EXAMPLE 2

A 10% solution of sodium tungstate at pH 12.6 was coated onto one surface of a Negev Institute cation exchange membrane. The treated surface was then pressed against a Negev Institute anion exchange membrane under heat. The potential difference across the composite bipolar membrane was 1.0 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm^{-2} . The current efficiency for acid base production was greater than 85%. The voltage across an untreated membrane formed from the same unipolar membranes, for the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 3

A 10% solution of potassium chromate at pH 12.9 was brushed onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were then pressed together. The potential difference across the composite bipolar membrane was 1.3 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm^{-2} . The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane, formed from the same unipolar membranes, for the same current and electrolyte compositions, was 3 volts.

EXAMPLE 4

A 10% chromium chloride solution (pH 12.4) was brushed onto a surface of both a Negev Institute anion exchange and an Asachi Chemicals cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.4 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm^{-2} . The current efficiency for acid base production exceeded 85%. The potential difference across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 5 volts.

EXAMPLE 5

Negev Institute anion and cation exchange membranes were dipped into a 10% sodium metasilicate solution (pH 8.0) at 90°C . The membranes were then pressed together. The potential difference across the composite membrane was 1.0 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm^{-2} . The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte

concentrations was 3 volts.

EXAMPLE 6

5 A 5% solution of nickel chloride (pH 12.7) was coated onto a surface of both a Negev Institute anion exchange membrane and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The voltage across the composite bipolar
10 membrane was 1.2 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated mem-
15 brane formed from the same unipolar membranes, for the same current and electrolyte concentrations was 3 volts.

EXAMPLE 7

20 A 5% solution of potassium chlorate (pH 2.4) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The
25 potential difference across the composite bipolar membrane was 1.4 volts at room temperature when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded
30 85%. The voltage across an untreated membrane formed from the same unipolar membranes for the same current and electrolyte concentrations was 3 volts.

EXAMPLE 8

35 A 10% solution of sodium phosphate at pH 13.6 was coated onto the surfaces of Negev Institute anion and cation exchange membranes. The membranes were then pressed
40 together to form a bipolar membrane. The potential difference across the bipolar membrane was 1.3 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current effi-
45 ciency for acid base production was greater than 85%. The voltage across an untreated membrane formed from the same unipolar membranes, for the same current and electro-
50 lyte compositions, was 3 volts.

EXAMPLE 9

A 5% solution of ruthenium chloride at pH 2.6 was brushed onto a surface of both a
55 Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were then pressed together. The potential difference across the composite bipolar membrane was 1.0 volts when it sepa-
60 rated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an un-
65 treated membrane formed from the same unipolar membranes, for the same current and electrolyte compositions, was 3 volts.

EXAMPLE 10

A 10% solution of indium sulphate (pH = 1.9) was coated onto a surface of both
70 a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were then pressed together. The potential difference across the composite bipolar membrane was 1.1 volts when it sepa-
75 rated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an un-
80 treated membrane, formed from the same unipolar membranes, for the same current and electrolyte concentrations was 3 volts.

EXAMPLE 11

A mixture consisting of equal volumes of a
85 10% sodium sulphate solution (pH 8.1) and a 10% calcium chloride solution (pH 7.6) was coated onto a surface of both a Negev Institute anion exchange membrane and a Negev Institute cation exchange membrane. The
90 treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.5 volts at room temperature when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current
95 efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

100

EXAMPLE 12

A mixture consisting of equal volumes of a
10% cerrous sulphate solution and a 10% sodium chromate solution was brushed onto a
105 surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were then pressed together. The potential difference across the composite bipolar membrane was
110 2.0 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base poroduction exceeded 85%. The voltage
115 across an untreated membrane, formed from the same unipolar membranes, for the same current and electrolyte compositions, was 3 volts.

EXAMPLE 13

120 A 5% solution of rhodium chloride at pH 10.1 was coated onto one surface of a Negev Institute cation exchange membrane. The treated surface was then pressed against a Negev Institute anion exchange membrane.
125 The potential difference across the composite bipolar membrane was 2.2 volts when it sepa-
130 rated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². the current efficiency for acid base production was greater than 85%. the voltage across an un-

treated membrane formed from the same unipolar membranes, for the same current and electrolyte concentrations, was 3 volts.

5 EXAMPLE 14

A mixture consisting of equal volumes of a 7% copper sulphate solution (pH 4.2) and a 10% potassium tetraborate solution (pH 10.4) was coated onto a surface of both a Negev Institute anion exchange membrane and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 2.3 volts at room temperature when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 15

A mixture consisting of equal volumes of a 7% thorium nitrate solution (pH 1.3) and a 5% potassium chloropalladate solution (pH 3.6) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane at room temperature was 1.7 volts when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

40 EXAMPLE 16

A mixture consisting of equal volumes of a 10% potassium chromate solution (pH 9.2) and a 5% manganous sulphate solution (pH 4.2) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.5 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, for the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 17

60 A mixture consisting of equal volumes of 10% zirconium chloride solution (pH 1.1) and a 10% sodium carbonate solution (pH 12.0) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated

surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.7 volts and it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, for the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 18

A mixture consisting of equal volumes of a 7% thorium nitrate solution (pH 1.3) and a 10% sodium carbonate (pH 11.5) solution was coated onto a surface of both a Negev Institute anion exchange membrane and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.1 volts at room temperature, when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes at the same current and electrolyte concentrations was 3 volts.

95 EXAMPLE 19

A mixture consisting of equal volumes of a 5% zirconium chloride solution (pH 0.7) and a 10% sodium molybdate solution (pH 6.8) was coated onto a surface of both a Negev Institute anion exchange membrane and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.2 volts at room temperature, when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes at the same current and electrolyte concentration was 3 volts.

EXAMPLE 20

A mixture consisting of equal volumes of a 5% zirconium chloride solution (pH 0.8) and a 5% sodium metaborate solution (pH 8.5) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.4 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes at the same current and electrolyte concentrations was 3 volts.

EXAMPLE 21

A mixture consisting of equal volumes of a 7% thorium nitrate solution (pH 1.3) and a 5% potassium chloroplatinite (pH 6) solution was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.0 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 22

A mixture consisting of equal volumes of a 7% solution of thorium nitrate (pH 2.3) and a 7% solution of sodium orthovanadate (pH 13.8) was coated onto a surface of both a Negev Institute anion exchange membrane and a Negev Institute cation exchange. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.4 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 23

A mixture consisting of equal volumes of a 5% stannous chloride solution (pH 0.7) and a 10% sodium dihydrogen phosphate solution (pH 4.6) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.3 volts at room temperature when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 24

A mixture consisting of equal volumes of a 0.7% sodium tellurate solution (pH 12.7) and a 5% stannous chloride solution (pH 0.7) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.5 volts when it separated 1M KCl solutions at room temperature and the

current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, for the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 25

A mixture consisting of equal volumes of 75 titanous chloride solution (pH 0.8) and a 10% solution of sodium chromate (pH 9.2) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential differences across the composite bipolar membrane was 1.9 volts at room temperature when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 26

A mixture consisting of equal volumes of a 10% sodium tungstate (pH 9.6) solution and a 10% cadmium chloride solution (pH 5.6) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.7 volts when it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, for the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 27

A mixture consisting of equal volumes of a 110 5% stannous chloride solution (pH 0.7) and a 4% sodium tellurate solution (pH 12.7) was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 1.5 volts when it separated 1M KCl solutions at room temperature and the 120 current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

EXAMPLE 28

A mixture consisting of equal volumes of a 7% lanthanum chloride solution (pH 4.7) and 130 a 10% sodium carbonate solution (pH 12.0)

- was coated onto a surface of both a Negev Institute anion exchange and a Negev Institute cation exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane at room temperature was 2.2 volts when it separated 1M KCl solutions and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 85%.
- 10 The voltage across an untreated membrane formed from the same unipolar membranes, at the same current and electrolyte concentrations, was 3 volts.

15 EXAMPLE 29

- A mixture consisting of equal volumes of a 5% stannous chloride solution (pH 0.7) and a 10% sodium dihydrogen phosphate solution (pH 4.6) was coated onto a surface of both a
- 20 Negev Institute cation exchange and an Ionics AR 103 anion exchange membrane. The treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 3.5 volts when it separated
- 25 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current efficiency for acid base production exceeded 70%. The voltage across an untreated membrane formed from the same unipolar membrane, for the same current and electrolyte
- 30 concentrations, was 7 volts.

EXAMPLE 30

- A mixture consisting of equal volumes of
- 35 7% thorium nitrate solution (pH 1.3) and a 10% sodium metasilicate solution (pH 13.0) was coated onto a surface of both a Negev Institute anion exchange and an Ionac MC-3142 cation exchange membrane. The
- 40 treated surfaces were pressed together. The potential difference across the composite bipolar membrane was 3.6 volts and it separated 1M KCl solutions at room temperature and the current was 100 mA cm⁻². The current
- 45 efficiency for acid base production exceeded 85%. The voltage across an untreated membrane formed from the same unipolar membranes, for the same current and electrolyte
- 50 concentrations, was 9 volts.

50 EXAMPLE 31

- A 10% solution of sodium metasilicate at pH 12.6 was coated onto one surface of a Negev Institute anion exchange membrane.
- 55 The treated surface was then pressed against a Tokuyama Soda C66-5T cation exchange membrane. The potential difference across the composite bipolar membrane was 2.2 volts when it separated 1M KCl solutions at room
- 60 temperature and the current was 100 mA cm⁻². The current efficiency for acid base production was greater than 80%. The voltage across an untreated membrane formed from the same unipolar membranes, for the
- 65 same current and electrolyte concentrations,

was 4.5 volts.

Although the invention has been described above with reference to drawings, preferred embodiments and specific examples, it will be appreciated that the invention is not limited thereto or thereby, and that variations are possible without departing from the spirit or scope of the invention as broadly described.

75 CLAIMS

1. A process for preparing bipolar membranes comprising joining together separate anion and cation exchange membranes characterized in that the interface of the said
- 80 membranes is chemically treated to introduce one or more inorganic compounds into the interface of the membranes.
2. A process according to claim 1, wherein a surface of at least one of said
- 85 membranes is coated with said one or more inorganic compounds prior to joining said membranes together.
3. A process according to claim 2, wherein said surface of at least one of said
- 90 membranes is coated with an aqueous solution containing said one or more inorganic compounds.
4. A process according to claim 1, wherein said one or more inorganic com-
- 95 pounds comprises one or more cations from Group 1a through to Group 4a, or from the lanthanide or actinide groups of Periodic Table of Elements.
5. A process according to claim 1,
- 100 wherein said one or more inorganic compounds comprises one or more anions selected from the group comprising tetraborate, metaborate, silicate, metasilicate, tungstate, chlorate, phosphate, sulphate, chromate, hydroxyl, carbonate, molybdate, chloroplatinate, chloropaladite, orthovandate and tellurate.
6. A bipolar membrane comprising an anion exchange region, a cation exchange region, and an interfacial region containing
- 110 one or more inorganic compounds and which comprises the surfaces of both said anion and cation exchange regions and the intervening regions therebetween.
7. A bipolar membrane according to claim
- 115 6, comprising separate anion and cation exchange membranes and an interfacial region comprising the surface layers of both membranes and the intervening region where they are contiguous.
8. A bipolar membrane according to claim
- 120 7 wherein the anion and cation exchange membranes contain sulfonic acid and/or quaternary ammonium groups.
9. A bipolar membrane according to claim
- 125 6 or claim 7 wherein the interfacial region contains one or more inorganic compounds comprising one or more cations from Group 1a through to Group 4a, or from the lanthanide or actinide groups of the Periodic Table of
- 130 Elements.

10. A bipolar membrane according to claim 9 wherein said one or more cations are selected from the group comprising: Thorium, Zirconium, Iron, Lanthanum, Cobalt, Cadmium, Manganese, Cerium, Molybdenum, Nickel, Copper, Chromium, Ruthenium, Rhodium, Stannous, Titanium and Indium.
- 5 11. A bipolar membrane according to claim 6 or claim 7, wherein the interfacial group contains one or more anions selected from the group comprising tetraborate, metaborate, silicate, metasilicate, tungstate, chlorate, phosphate, sulphate, chromate, hydroxyl, carbonate, molybdate, chloroplatinate, chloro-
- 10 15 paladite, orthovandate and tellurate.

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